Polymeric Surfactant Additive from Natural Starch for the Reduction of Environmental Pollution

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Abstract- **The surfactant-like chemical contamination of water from a wide range of toxic derivatives, in particular soap, surfactants, heavy metals, aromatic molecules and dyes, is a serious environmental problem owing to their potential human toxicity. Therefore, there is a need to develop natural polymeric surfactant from starch that can free from toxic pollutants found in wastewaters, ponds, drains, canals and rivers. Among all the treatments proposed, adsorption is one of the more popular methods for the removal of pollutants from the waste water and soap-detergent free water. On the other hand, water living organism can live smoothly without chemically substances (soap, surfactants) in the mentioned sources by using naturally polymeric surfactants (prepared from potato starch). The main objective of this review is to provide recent information about the most important features of these polymeric materials and to show the advantages gained from the use of adsorbents containing modified biopolymers in waste water treatment where chemical substances (surfactant like CTAB, Tween-20, SDS) mixing when they are used as washing purposes in textile industries. From the experimental results of viscosity, surface tension and other physical properties it indicated that adding starch in detergent as soap filler these properties have changed which also indicated the more washing activity of polymeric starch (potato) were cheaply available indoor market in Bangladesh. Biodegradable starch interactions with ionic surfactants (CTAB, SDS) by the way of H-bond formation to ensure complexation and reduced the harmful criteria of living organism in water also to ensure maximum protection of water pollution compared with chemically detergent. The formed complexes from starch-ionic surfactant-water were analyzed and characterized by XRD and SEM instruments. Some of the complexes exhibited excellent emulsifying efficiency and polymeric surfactants performance properties with this biodegradable natural starch polymer.**

Keywords- Polymeric surfactant, CMC, Natural Potato Starch, SEM, surfactants, water pollution

I. INTRODUCTION

Water pollution due to toxic metals such as soluble soap-detergents in water in ponds, rivers, canals and organic compounds remains a serious environmental and public problem Moreover, faced with more and more stringent regulations, water pollution has also become a major source of concern and a priority for most industrial sectors such as textile Industry, soap Industry, detergent Industry. Heavy metal ions, aromatic compounds (including phenolic derivatives, and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses. They are common contaminants in wastewater and many of them are known to be toxic or carcinogenic. For example, chromium (VI) is found to be toxic to bacteria, plants, animals and people [1]. Mercury and cadmium are known as two of the most toxic metals that are very damaging to the environment [2]. In addition, heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Therefore, their presence in the environment, in particular in water should be controlled. Chlorinated phenols are also considered as priority pollutants since they are harmful to organisms even at low concentrations. They have been classified as hazardous pollutants because of their harmful potential to human health [3,4]. 2,4,6-trinitro- toluene (TNT) is a nitro-aromatic molecule that has been widely used by the weapon industry for the production of bombs and grenades. This compound is recalcitrant, toxic and mutagenic to various organisms [5,6]. Many synthetic dyes, which are extensively used for textile dyeing, paper printing and as additives in petroleum products are recalcitrant organic molecules that strongly color waste water.

Strict legislation on the discharge of these toxic products makes it then necessary to develop various efficient technologies for the removal of pollutants from waste water. Different technologies and processes are currently used. Biological treatments [7–9], membrane processes [10–13], advanced oxidation processes [14–17], chemical andElectro chemical techniques [18–20], and adsorption procedures are the most widely used for removing metals and organic compounds from industrial effluents. Amongst all the treatments proposed, adsorption using sorbents is one of the most popular methods since proper design of the adsorption process will produce high-quality treated effluents. Polysaccharides, stere oregular polymers of mono saccharides (sugars), are unique raw materials in that they are: very abundant natural polymers (they are referred to as biopolymers); inexpensive (low-cost polymers); widely available in many countries; renewable resources; stable and hydrophilic biopolymers; and modifiable polymers. They also have biological and chemical properties such as non-toxicity, biocompatibility, biodegradability, poly functionality, high chemical reactivity, chirality, chelation and adsorption capacities. The excellent adsorption behavior of polysaccharides is mainly attributed to: (1) high hydrophilicity of the polymer due to hydroxyl groups of glucose units; (2) presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups); (3) high chemical reactivity of these groups; (4) flexible structure of the polymer chain. From the above mentioned features, it is proved that many researchers have paid their attention on this field. In spite of half century of great effort, many academic aspects such as, chemistry, chemical reactions, bond formation on starch-surfactants interaction are still open for discussion. The purpose of the present investigation is to explore the effect of starch interaction with various surfactants and the better understanding the mechanism between starch and surfactants complexes formed as polymeric surfactants studied by the ternary phase diagram, interfacial surface tension and viscosity measurement and characterized by the XRD and SEM analysis.

II. EXPERIMENTAL

A. Materials

Potato starch as powder form was purchased from UNI-CHEM, China and its degree of substitution (DS) was 0.80. Starch solution was prepared by heating the starch in water in an autoclave at 120^0C for 30 min. All solutions were prepared at least 24 h before measurement was performed. The surfactants sodium dodecyl sulphate (SDS), N-cetyl- N,N,N-trimethyl ammonium bromide (CTAB) and Tween-20 were purchased as analytical grade and were used without further purification. The water used was ion exchanged and distilled. Its conductivity, and reduced viscosity were 2.0µs and 4.0 dm^3/mol, respectively and its surface tension was 71.5×10^{-3} ± 0.5 N/m at 30^0C. All other chemicals were analytical grade and were used without further purification. All the chemicals from a real source which is analytical grade purchase from Loba Chemicals, India,

Viscisity: Viscosities were determined with an Ostwald viscometer according to British standard (Fisher Scientific TM 200) with a fluctuation of ± 0.1^0 C was used. The flow of time was recorded by a timer accurate up to ± 0.01 second. At certain surfactant/starch ratios the aggregates formed were very mobile flocks, which tended to form in the samples. This could be partly avoided by draining the capillary fully between measurements.

B. Characterization

SEM analysis

Scanning Electron Microscope (SEM, JEOL, JSM 6301F, Japan), Fine coaster (JFC 1200, JEOL, Japan), Aluminum specimen stub, Double-sided adhesive tape.

Surface tension

Surface tension was measured with a drop weight method (Stalagmometer i nstruments). In the calculation of surface tension, the correction factors of Huh and Mason [65] were used. The reproducible result between measurements of the same sample was ±0.5 mN/m. The results of the surface tension measurement were presented as

(γ) values calculated from. where, f is equal to , v is the volume of the drop and r is its radius, mg is the weight of falling drop and γ is its surface tension. A drop of the weight (mg) given by the above equation has been d esignated as the ideal drop. Repeated measurements (2-4 times) were conducted on each sample from which equilibrium surface or interfacial tension values were obtained by averaging the values at very long periods, where the surface and interfacial tension values showed little or no change with time. Prior to normal value.

Procedure for sample determination

Scanning Electron Microscope (SEM) of potato starch, surfactant sample and starch-surfactant complexes samples were less than 4% moisture content before examined. Dried sample and sprinkle were taken onto the double-sided adhesive tape attached to the specimens tub. The excess sample was removed and the sample was placed in fine coater of gold coating for150seconds. The coated sample was then placed in the sample chamber of the SEM .The sample was examined at magnification of 2,500 and 6,000 with the accelerating voltage of 10 Kv.

III. RESULTS AND DISCUSSIONS

Some of the prepared starch-surfactant mixture lowered the reduced viscosity and surface tension of water, namely at lower concentration of the sample (**Table I & II**). The functional properties of some of the prepared surfactant and starch mixed surfactant solutions were tested for emulsifying efficiency, washing power and anti re-depositiative efficiency. The emulsifying efficiency was characterized by the stability of the parafinic Tween-20/water emulsions and other surfactant mixture at definite ratio. The results of reduced viscosities in CTAB and SDS summarized in Table 2 and 3 which show that some of the surfactant made emulsions of the oil/ water type stable even after 24 h. Their efficiency was comparable to that of the commercial emulsifier Tween-20. Some of the tested mixture showed excellent washing power exceeding that of the anionic detergent, name SDS containing dodecyl chains. But compared with Tween-20 as a non-ionic surfactant absence of H-bonding with potato starch (Fig. I & II) showed the real fact of interactions by forming H-bonding with ionic surfactant(SDS,CTAB)

Table I: Reduced viscosity of Starch and surfactant mixture of CTAB and SDS with starch

Temp °C	Reduced Viscosity (polymer)					reduced Viscosity (polymer-surfactant mixture)				
	0.0625%	0.125%	0.250%	0.500%	1.000%	0.0625%	0.125%	0.250%	0.500%	1.000%
25	1644.528	813.616	411.320	213.134	116.297	1549.392	912.256	539.508	298.854	182.692
35	1385.072	823.416	481.496	288.598	170.153	1298.592	786.768	454.012	240.734	159.576
45	1229.392	718.792	426.532	247.572	151.884	1177.504	703.104	392.944	216.802	135.538
55	1065.072	645.592	374.624	218.512	133.615	1021.824	608.992	344.088	192.870	125.923
65	926.688	572.392	341.036	201.418	121.115	918.048	541.016	307.448	168.940	108.615
75	857.504	525.328	313.556	184.324	110.538	822.912	488.728	279.968	155.264	99.961
85	771.024	478.272	286.076	168.94	99.961	753.728	441.672	252.488	141.588	90.346

Table.II The surface tension of aqueous solution of Cetyltrimethyl ammonium bromide (CTAB) with different amounts of added starch solu tion (%)

Concentration of Starch solution X10^{-2}	Log concentration of Starch solution (%)	Surface tension of CTAB solution (N/m)×10^{-3}			
		0.05%	0.10%	0.15%	0.20%
1.00	-2.00	50.00	49.56	49.41	48.86
2.00	-1.69	49.30	49.06	48.12	48.00
3.00	-1.52	48.80	48.58	47.96	47.83
4.00	-1.39	48.61	48.34	47.90	47.76
5.00	-1.30	48.48	48.28	47.88	47.67
6.00	-1.22	48.42	48.20	47.82	47.52
7.00	-1.15	48.42	48.20	47.80	47.52
8.00	-1.09	48.40	48.20	47.80	47.50
9.00	-1.04	48.40	48.20	47.80	47.50
10.00	-1.00	48.90	48.70	48.50	48.20

Table-III Determination of surface tension of starch mixed surfactant (CTAB & SDS) 0.15%solution at different temperature (Ranges: 30-75°C)

Temperature. (°C)	Conc. Of starch mixed surfactant (CTAB) solution	Surface tension (N/m)×10^{-3}	Conc. Of starch mixed surfactant (SDS) solution	Surface tension (N/m)×10^{-3}
30	0.15%	47.90	0.15%	49.60
35	0.15%	47.02	0.15%	48.58
40	0.15%	46.22	0.15%	46.64
45	0.15%	44.62	0.15%	45.40
50	0.15%	44.02	0.15%	43.92
55	0.15%	42.82	0.15%	44.02
60	0.15%	41.34	0.15%	41.56
65	0.15%	41.10	0.15%	41.50
70	0.15%	41.06	0.15%	41.50
75	0.15%	41.06	0.15%	41.50

The anti-redepositive efficiency was higher than the starting SDS, but moderate in comparison to starch used as a co-builder in detergents [64]. in case of ionic surfactant (SDS, CTAB) the changing is remarkable due to maximum interactions occurred with starch polymer. Here, we mentioned that temperature has a remarkable effect in the complexes of starch-ionic surfactant, here it is obtained according to Arrhenius rule increasing temperature reduced viscosity and specific viscosity is reduced due to the freeness of solution which has been seen in Table I and increasing temperature the surface tension value is decreasing in tab-III.

B. Scanning Electron Microscopy (SEM)

Figs. 1a, 1b and 1c show the individual surface image of starch, SDS and starch-SDS mixture, respectively studied by SEM. It can be seen from Figs. 1a, 1b and 1c that the surface images of the starch and surfactant are quite different from each other. The surfaces of the starch, SDS and mixture of these two looks like granules, pop-corn and needle like respectively. It is clear that, at a certain temperature and concentration, the starch interacts with the surfactant through the formation of H-bonds and changes its surface structure.

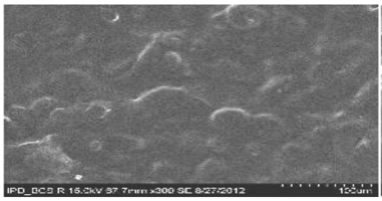

Fig.1 (a) starch

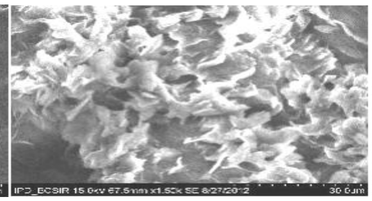

Fig.2 (b) Surfactant (SDS)

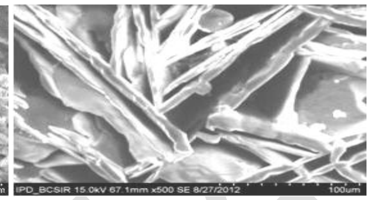

Fig.3 (C) starch with SDS mixture

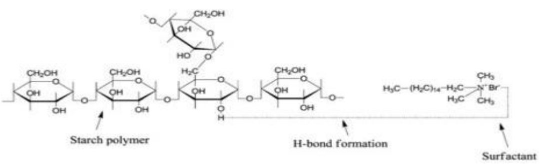

Fig. 2: H-Bond formation starch with cationic surfactants.

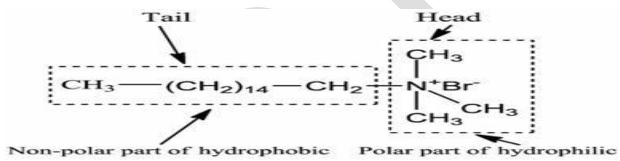

Fig. 3: Only cationic surfactant molecule.

From fig. 2 and fig. 3, it can be seen that starch molecule have many hydroxyl groups and hydrogen atoms which bind with surfactant molecule through H-atom called H-bond formation. So bond break down is easily of hydrophilic and hydrophobic parts of surfactant molecule, finally cleansing activity increased although starch are biodegradable and eco-friendly. XRD Figures 4, 5 and 6 has been given below for better understanding starch, SDS, CTAB complexes as variation of concentration.

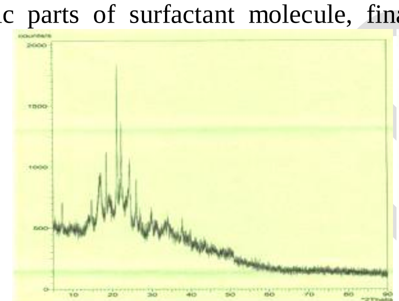

Fig. 4 Starch XRD

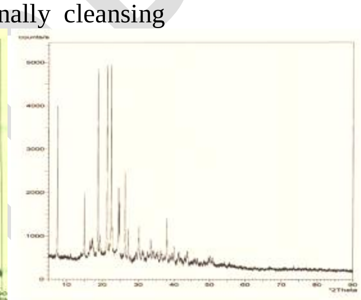

Fig. 5 Starch-SDS complexes XRD

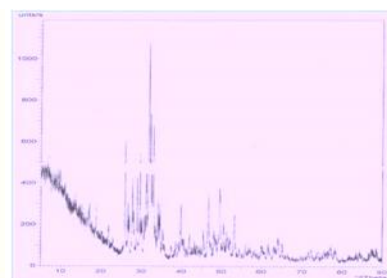

Fig.6 Starch-CTAB complexes XRD

The interactions between starch and all type of surfactants and their mixtures were studied by using surface tension, solution viscosity measurements and to do the ternary phase diagram, FT-IR analysis for H- bond detection and identification , SEM analysis for characterization for smoothness of surfaces and XRD analysis for crystallization of complexes structure. The composition and structure of the complexes of starch and surfactants mixture were studied by using phase equilibrium determination, Scanning electron microgram (SEM) and X-ray diffraction (XRD) measurements. Critical association concentrations (cac) are well below the critical micellization concentrations (CMC) of the surfactants. Associative phase separation occurs in extremely dilute systems when the charge ratio between the surfactants and the polymer is close to one. The effect of mixing on micellization of the binary surfactant solution can be described by taking into account the effects of the volume difference between the hydrocarbon chains.

IV. CONCLUSION

The investigations presented in this paper show that strong ionic interaction occurs between cationic and anionic surfactants (CTAB, SDS) except nonionic surfactant (Tween-20) and starch polymer. Complex formation on starch depends on the chain length difference in exactly in the same way as for free mixed micelles .The separated complex phase is a hydrophobic, highly viscous and gel like containing 40 to 60% water. The highly and low water content of the complex phase indicates that the interactions between the starch and ionic surfactants are very strong and they are capable more effective washing properties in textile industry, dish wash in household, garments and laundry shops than normal chemical detergent available in our indoor market which is harmful of water living organism, insects, fishes and other animals living in water. The polymeric surfactants which are newly prepared from potato starch is also biodegradable and eco-friendly for environment not only this, the natural surfactant from natural sources help our green chemistry and safe for water living organism due to washable surfactant from polymeric potato starch where small amount of chemical detergents also present . This research will help to keep our water living fishes and other water pollutant carrying materials free, due to small amount of chemical detergent is used with this polymeric surfactant derived from potato starch as soap or surfactant additives.

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